

Microstructure and surface impurity segregation in Al-substituted $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$

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One of the important challenges for further development of Li-batteries is to increase the practical energy density. Successful use of lithium metal as the anode material in rechargeable batteries would enable a very high energy density device especially when coupled with high capacity cathodes such as air and sulfur [^{1,2}]. There are severe safety concerns due to the extreme reactivity of metallic lithium with most liquid electrolyte solutions. Use of a solid electrolyte is considered one way to enable metallic lithium electrodes given that the criteria of high conductivity and good chemical stability are met. Among various solid electrolytes, the garnet structure $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ (LLZO) is promising due to its fast ionic transport [³] (conductivity $>10^{-4}\text{S/cm}$ at room temperature) and good chemical stability against metallic lithium [⁴].

Generally, high density and phase pure materials are favored for solid electrolyte applications because of better conductivity and mechanical integrity. A typical sintering process of LLZO requires pellets covered by the same mother powder at a temperature as high as 1230°C for more than 30 hrs to densify [3]. Usually, the pellet is sintered but there are porous regions that are not completely densified [⁵]. This lowers the total conductivity and increases the risk of lithium dendrite penetration through the porous regions during cycling, which may lead to an electrical short. High temperature and long sintering time may result in impurity formation, especially due to lithium loss at high temperature and Al incorporation when alumina crucibles are used. High density LLZO (97%) without a LaAlO_3 impurity has been successfully fabricated by hot-pressing at 1000°C [⁶].

In this work, we studied the morphology change with respect to grain size, and impurity formation during the sintering of the Al-substituted LLZO cubic phase under various processing conditions. Specifically, by controlling the particle size, we have been able to sinter cubic LLZO to a relative density of 94% with $100\text{-}200\mu\text{m}$ grain size (Fig. 1) at a considerably lower temperature than previously achieved by the classic ceramic processing techniques. We also investigated the microstructure and surface impurity formation of the same pellets sintered under different LLZO powder cover. Laser induced breakdown spectroscopy was adopted to map the distribution of impurities in these samples (Figure 2). Our results show that particle size control is critical to successful densification and that the chemical composition of the powder cover strongly affects morphology and impurity formation in the sintered pellets. These properties, in turn, affect the electrochemical behavior.

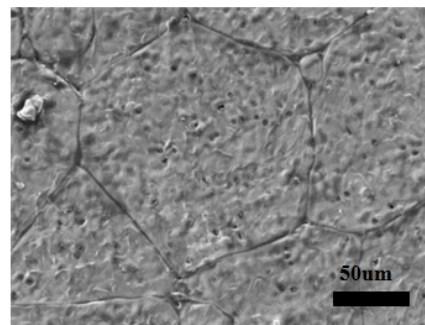


Figure 1. SEM surface image of a densified LLZO pellet

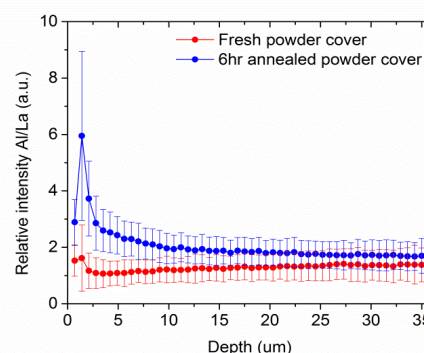


Figure 2. Al/La signal intensity ratio as a function of depth in samples with two different powder covers.

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